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COLUMBIA UNIV NEW YORK DEPT OF CHEMISTRY
STRUCTURAL AND DYNAMIC STUDIES OF MATERIALS POSSESSING HIGH ENERGETICS (U)
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"Solvent Sensitivity of Type II Photoreactions of Ketones as a Device to Probe Solute Location in Micelles", N.J. Turro, K.C. Liu and M.-F. Chow, Photochem. Photobio., 26, 413 (1977).

"Energy Acquisition, Storage, and Release. Photochemistry of Cyclic Azoalkanes as Alternate Entries to the Energy Surfaces Interconnecting Norbornadiene and Quadricyclene," N.J. Turro, W.R. Cherry, M.F. Mirbach and M.J. Mirbach, J. Am. Chem. Soc., 99, 7388 (1977).

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This final report updates and summarizes the research accomplished under this Grant during the period of November 1, 1977 through October 31, 1980. We have emphasized investigations in the following areas: (1) Reactivities and efficiencies of reaction of singlet oxygen with organic compounds; (2) Reaction of singlet oxygen with strained organic molecules; (3) Generation of singlet oxygen in a molecular beam; (4) Generation and dynamic analysis of reactive diradicals, such as trimethylene methanes and carbenes in fluid solution. These studies are			

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intended to advance our knowledge of the nature and behavior of excited molecules and their emission characteristics. We have elucidated the available mechanisms for producing excited molecules selectively and in high yield via chemiluminescent reactions. Our investigation of singlet oxygen chemistry and chemiluminescent reactions may lead to the development of novel chemical lasers and of means of protecting polymers against oxidative degradation.

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A major goal of the research supported by this grant was the advancement of our knowledge of the nature and behavior of molecules possessing an exceptionally high energy content. Both triplet (ground state) molecular oxygen, $^3\text{O}_2$, and singlet (excited state) molecular oxygen, $^1\text{O}_2$, were studied. We employed product analysis, structure-reactivity relationships, chemiluminescence methods, and laser flash spectroscopy to assist in the establishment of mechanisms that provided an understanding of these oxidations. We extended our chemiluminescent methods to include pulsed generation of chemiluminescent species. For example, we examined potential precursors for the pulsed laser excitation of $^1\text{O}_2$. We also concluded a series of investigations of the generation and reactions of $^1\text{O}_2$ in polymer films. We are extending these studies to include oxidations on selected surfaces such as porous glass and silica. Finally, we discovered that applied laboratory magnetic fields can significantly influence reactions which generate $^1\text{O}_2$. We are now investigating whether the reactions of $^1\text{O}_2$ are significantly influenced by a magnetic field.

AFOSR Program Manager: Dr. Anthony Matuszko

10. FINAL REPORT OF RESEARCH ACCOMPLISHMENTS SUPPORTED BY GRANT AFOSR-78-3502
DURING THE THREE YEAR PERIOD 1 NOVEMBER 1977 TO 31 OCTOBER 1980.

The research supported by this Grant has provided information that impacts on a number of areas that are concerned with the structure and dynamics of materials possessing high energy content. Our major emphasis has been directed toward reactions associated with molecular oxygen (O_2) in its triplet ground electronic state (3O_2) and in its lowest energy singlet excited state (1O_2). Since many of the reactions of O_2 are accompanied by chemiluminescence, we have developed a range of strategies and techniques for the detection and analysis of chemiluminescent reactions.

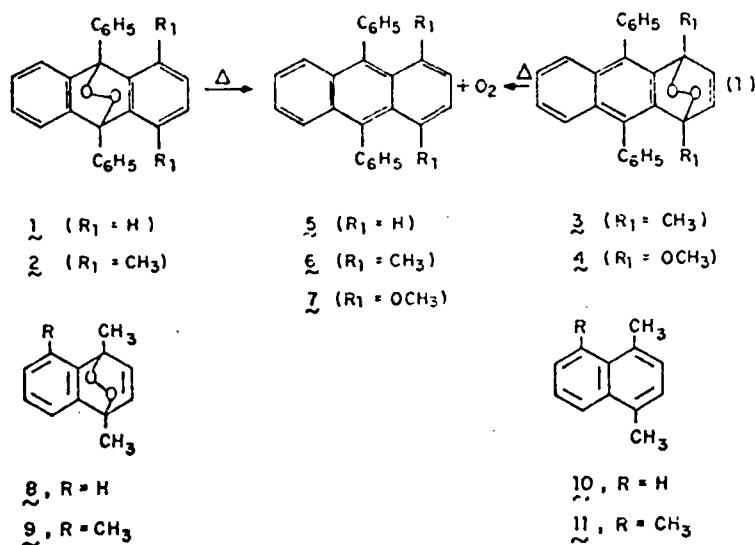
The following topics of research have been investigated: (1) The thermolysis of endoperoxides to produce molecular oxygen; (2) The diffusivity and reactivity of molecular oxygen polymer films; (3) The measurement of rate constants and efficiency of reaction of singlet oxygen with materials of high energy content; (4) The reactions of triplet and singlet molecular oxygen with strained molecules such as ketenes and acetylenes; (5) The chemiluminescence produced by the reaction of molecular oxygen with carbenes; (6) The measurement of the dynamics of intersystem crossing of carbenes (in collaboration with Professor K.B. Eisenthal).

Thermolysis of Naphthalene and Anthracene Endoperoxides to Produce Singlet Oxygen.

The thermolysis of a series of naphthalene and anthracene endoperoxides has been investigated (shown in Scheme I). Each compound studied decomposes quantitatively into molecular oxygen and the corresponding aromatic compound. The activation parameters for these thermolyses and the primary yield of 1O_2 were measured. From our data, especially a comparison of ΔS^\ddagger and the 1O_2 yields, we conclude that two classes of mechanisms operate. The first class (small or

negative ΔS^\ddagger , high yield of $^1\text{O}_2$) involves a concerted pathway which does not possess an efficient mechanism for intersystem crossing anywhere along the reaction coordinate. In the second class (ΔS^\ddagger large, positive, low yield of $^1\text{O}_2$) the C-O bond breakage leads along the reaction pathway and a mechanism for effective intersystem crossing is present along the reaction pathway. Energetics are unable to explain the reduced efficiency of $^1\text{O}_2$ formation.

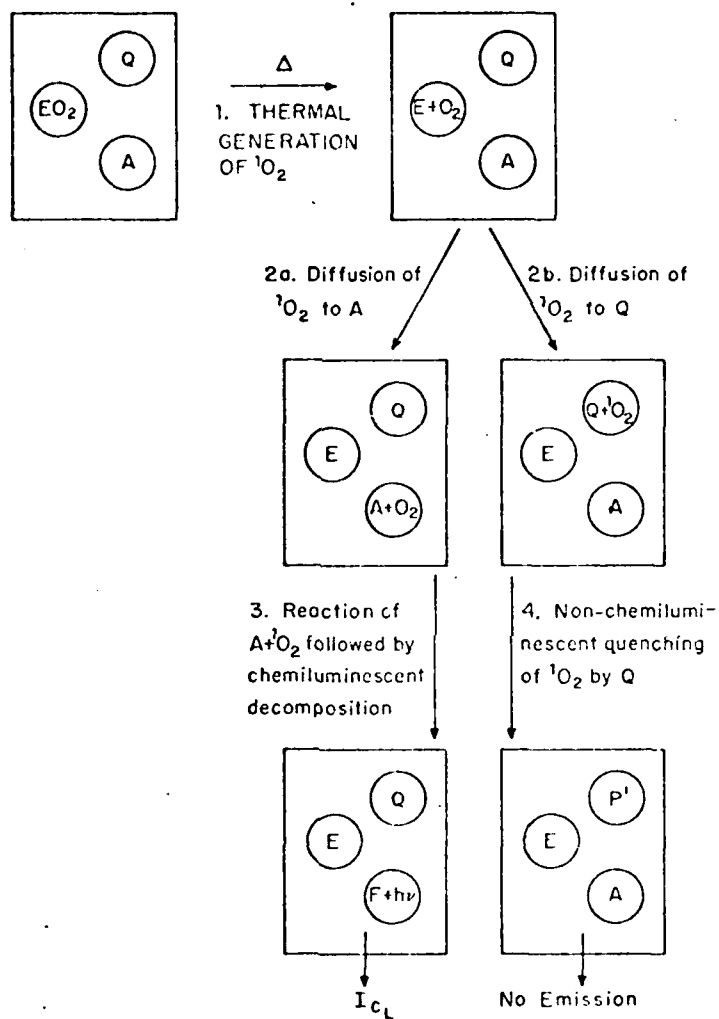
Scheme I. Endoperoxides investigated.



Diffusivity and Reactivity of Singlet Oxygen in Polymers.

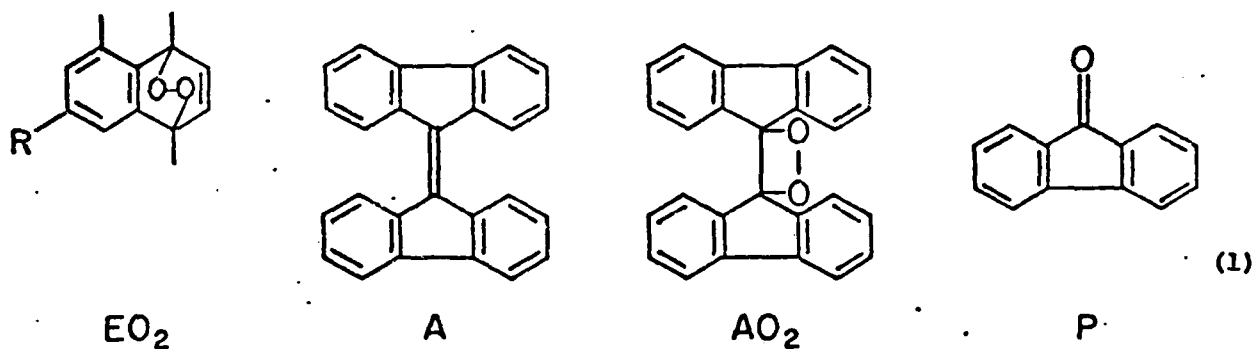
A chemiluminescence procedure for generating and detecting singlet oxygen ($^1\text{O}_2$) in polymer films (polystyrene and polymethylmethacrylate) has been developed (Scheme II). The method involves the production of $^1\text{O}_2$ from naphthalene endoperoxides (EO_2), followed by diffusion of $^1\text{O}_2$ to an acceptor (A) which reacts with $^1\text{O}_2$ to form a chemiluminescent product ($\text{AO}_2 \rightarrow \text{P} + \text{h}\nu$). The structures involved are shown in Eq. 1. Measurement of the resulting chemilu-

Scheme II. Schematic description of the system employed to measure the diffusivity of $^1\text{O}_2$ in polymers.



minescence as a function of acceptor concentration provides information on the diffusivity and reactivity of $^1\text{O}_2$ in polymer films. A model based on the theory of exciton migration is employed to extract quantitative parameters from the data.

Addition of non-chemiluminescence quenchers results in Stern-Volmer quenching of chemiluminescence. Measurement of the quenching of chemiluminescence as a function of quencher concentration provides information on the efficiencies of quenchers toward deactivation of $^1\text{O}_2$ in polymer films. The results show that $^1\text{O}_2$ can diffuse 500-600 Å in polystyrene or polymethylmethacrylate films at room temperature.



- 1 R = H
2 R = CH_3

Rate Constants for Reaction of Singlet Oxygen with High Energy Content Molecules.

The rate constants for quenching of $^1\text{O}_2$ by various ethylenes possessing high energy content have been measured. The systems studied are intended to probe the relation between "strain" or "high energy content" and quenching efficiency (and/or reactivity). An important result is the observation that bis-adamantylidene (BA) is a very poor quencher relative to tetramethylethylene (TME). This demonstrates that the different chemistry of these tetrasubstituted ethylenes ($\text{BA} + ^1\text{O}_2 \rightarrow \text{dioxetane}$, $\text{TME} + ^1\text{O}_2 \rightarrow \text{ene product}$) results from the inhibition of the ene reaction, not an acceleration of the dioxetane reaction.

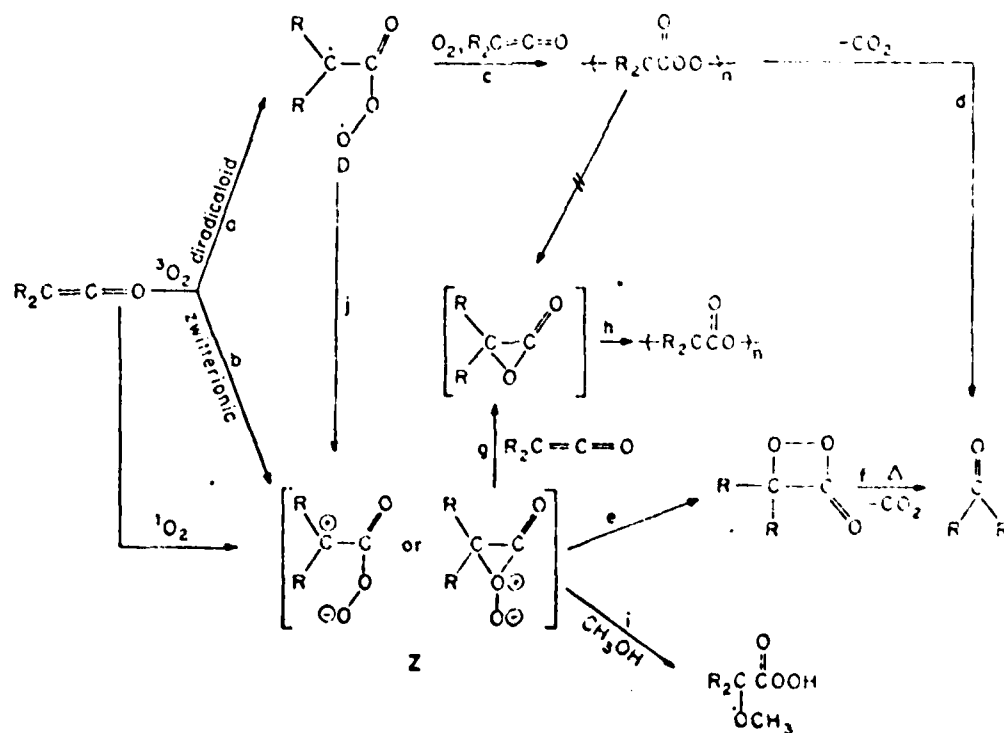
We have employed endoperoxides as a source of singlet oxygen in order to

establish (a) the efficiencies of chemical reactions involving $^1\text{O}_2$ and organic compounds and (b) to measure the rates of physical versus chemical quenching of organic compounds toward $^1\text{O}_2$. Since we now have sources that produce $^1\text{O}_2$ quantitatively, we can use our rate data for the total quenching constant to derive these important parameters. We also have found important magnetic field effects on the efficiency of $^1\text{O}_2$ production.

Reactions of Triplet and Singlet Molecular Oxygen with Strained Molecules.

An investigation of the reactions of ketenes with molecular oxygen ($^1\text{O}_2$ and $^3\text{O}_2$) has revealed that two mechanisms, one diradicaloid and one zwitterionic, occur in these oxidations (Scheme III). In the case of dimethyl ketene, diradicaloid pathways predominate, whereas for diphenyl ketene zwitterionic pathways predominate.

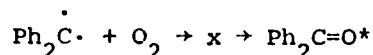
Scheme III. Reaction scheme for reaction of $^1\text{O}_2$ and $^3\text{O}_2$ with ketenes.



The reaction of $^1\text{O}_2$ with strained acetylenes has been investigated. At low temperatures, a chemiluminescent intermediate capable of decomposing to produce a 1,2-diketone is formed. This intermediate is likely to be the first example of a 1,2-dioxetane.

Chemiluminescent Reaction of Molecular Oxygen with Carbenes.

We have generated diphenyl carbene under various conditions (77K in a solid solution, ambient temperature in polymers and in fluid solution) and have investigated the chemiluminescent reaction of $\text{Ph}_2\dot{\text{C}}$ and O_2 :



The isolated major product of reaction is benzophenone. The observed chemiluminescence corresponds precisely to benzophenone phosphorescence. We have performed a number of initial experiments in which the rate of carbene disappearance has been studied by monitoring its ESR signal (at 77K), its fluorescence (at 77K and ambient temperature) and its absorption (at 77K and ambient temperature). At 77K we observe two decay pathways which we are now subjecting to a detailed kinetic analysis. At ambient temperature we have observed two transients after a 15 ns pulse from the 249 nm line of an Excimer laser. We have tentatively assigned the first transient as singlet diphenyl carbene which decays to the second transient triplet diphenyl carbene. If this assignment is correct, it would represent the first direct spectroscopic observation of diphenyl carbene singlet in fluid solution.

Dynamics of Intersystem Crossing of Diphenyl Carbene.

A combination of picosecond and nanosecond laser measurements, chemical quenching experiments and triplet sensitization experiments has allowed the determination of the rate of intersystem crossing of singlet diphenylcarbene

to triplet diphenylcarbene (k_{ST}) as well as the rate of reverse intersystem crossing process (k_{TS}) in acetonitrile at room temperature. The systems shown in Scheme IV were employed to sort out the singlet and triplet carbene chemistry. It is shown under the conditions for kinetic measurements that singlet and triplet diphenylcarbene (^1DPC and ^3DPC , respectively) are in rapid equilibrium relative to reactions, so that knowledge of the values of k_{ST} and k_{TS} allows determination of the equilibrium constant and free energy for the $^1\text{DPC} \rightleftharpoons ^3\text{DPC}$ process.

Scheme IV.

